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Ontario

Water Resources Paper 16

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ENHANCED GREAT LAKES TRIBUTARY MONITORING IN ONTARIO: 1980 WATER QUALITY STATUS REPORT

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Ref. 70962

WATER RESOURCES PAPER 16

ENHANCED GREAT LAKES TRIBUTARY MONITORING IN ONTARIO: 1980 WATER QUALITY STATUS REPORT

by

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Additional copies of this Water Resources Paper may be obtained in person from the Ontario Government Bookstore, 880 Bay Street, Toronto, Ontario or by mail from the Ontario Government Publications Centre, 5th Floor, 880 Bay Street, Toronto, M5S 1Z8.

ISSN 0708-4749
ISBN 0-7743-7857-3

Parts of this publication may be quoted if credit is given. It is recommended that reference to this report be made in the following form:

Eddie, J.D. and D.F. Onn, 1982. Enhanced Great Lakes Tributary Monitoring in Ontario: 1980 Water Quality Status Report; Ontario Ministry of the Environment, Water Resources Paper 16.

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ABSTRACT

The Enhanced Tributary Monitoring Program (ETMP) was initiated in 1979 and 1980 at 15 key Great Lakes tributary outlet monitoring stations to obtain a better data base, primarily by increased sampling frequencies; to improve the precision of tributary load estimates; and, to establish procedures to optimize future Great Lakes tributary sampling. Additional water-quality monitoring was undertaken at existing Provincial Water Quality Network (PWQN) stations with supplementary funding received from Environment Canada under the terms of the Canada/Ontario Agreement. This report documents the status of the enhanced monitoring; presents summaries of the monitoring data; and, recommends improvements for future enhanced monitoring.

Water-quality measurements and load estimates for the 1980 water year (October 1979 to September 1980) are presented for various water-quality parameters monitored at the 15 ETMP outlets. The precision of annual phosphorus loadings (i.e. expressed as the percentage of mean phosphorus load) improved as a result of the enhanced monitoring. For total phosphorus, the mean standard error for the 15 tributaries improved from 36.2% average for routine monthly monitoring to 8.09% average for the more frequent ETMP monitoring. Sampling requirements (i.e. frequency and distribution in time) for two, principal water-quality parameters (total phosphorus and nitrate-nitrogen) were found to be different for each monitored tributary.

Enhanced monitoring has continued to date and its future use will continue to allow the computation of precise tributary loads, and optimize future resource allocation by further site-specific refinements of sampling strategy (i.e. sample-collection frequency and distribution in time).

ACKNOWLEDGEMENTS

The authors wish to express their sincere thanks to Messrs. R. C. Ostry and R. D. Terry for their critical review of the manuscript and technical guidance throughout the program. The Ministry's Laboratory Services Branch and laboratory analysts in Toronto and Thunder Bay are acknowledged for their expertise in providing analytical data. Thanks are also extended to Ms. Mary Lou Fitzmaurice for the compilation of data and computer assistance.

The investigations described in this report were in part supported by funds received from Environment Canada under terms of the Canada/Ontario Agreement respecting Great Lakes Water Quality.

1.0 INTRODUCTION

This report documents the status of the Enhanced Tributary Monitoring Program; presents a summary of the monitoring data; and recommends improvements for future enhanced monitoring.

1.1 Background

The Ontario Ministry of the Environment (MOE) has been measuring water quality at strategic locations throughout Ontario since 1964 to monitor the effects of point-source waste-water discharges and those effects originating from various non-point source land uses. As part of the Ministry's contribution to the International Joint Commission's programs on the Great Lakes, computed estimates of phosphorus loadings from key Great Lakes tributaries located in Ontario are provided to, and reported annually by the Great Lakes Water Quality Board. Historically, these phosphorus loads were derived from a marginal water-quality data base, as the Provincial Water Quality Monitoring Network (PWQN) lacked the financial support to obtain frequent water samples during high-flow events. Supplementary funding received from Environment Canada under the terms of the Canada/Ontario Agreement allowed increased sampling of some stations in the existing Network. This sampling was initiated in 1979 and the results are discussed in this report. In addition to phosphorus, supplementary water-quality and sediment-quality monitoring was undertaken (see Table 2) to enable the computation of other contaminant loads. Sediment-quality measurements are the subject of a future report.

1.2 Objectives

The objectives of the Enhanced Tributary Monitoring Program are to obtain a better data base, primarily by increased sample frequencies; establish procedures to improve the precision of the tributary load estimates; and, to establish procedures to optimize future Great Lakes tributary sampling.

TABLE 1: WATERSHED PHYSICAL CHARACTERISTICS

Terminal Basin	Drainage Area in Canada (10^3 hectares)	Tributary	Tributary Drainage Area (10^3 hectares)	Percentage of Canadian Great Lakes Drainage Area	Mean Annual Flow 1980 Water Year cms	Hydrograph Category "natural" or "modified" (Section 2.2.2)
Lake Superior	8,350	Kaministikwia R.	782	9.4	44.2	modified
		Little Pic R.	132	1.6	16.6	natural
		Pic River	427	5.1	50.5	natural
		Black River	224	2.7	34.0	natural
		Sub Total	1,570	18.8	145.0	N/A
Lake Huron	8,720	Mississaugi R.	930	10.7	131.0	modified
		Spanish River	1,410	16.2	169.0	modified
		Saugeen River	396	4.5	63.0	natural
		Sub Total	2,740	31.4	363.0	N/A
Lake Erie	1,600	Sydenham River	320	20.0	25.7	natural
		Thames River	565	35.3	68.2	natural
		Grand River	694	43.4	77.1	natural
		Sub Total	1,580	98.7	171.0	N/A
Lake Ontario	3,090	Welland River*	-	-	28.2	modified
		Twelve-Mile Cr.*	-	-	200.0	modified
		Humber River	88.7	2.9	8.6	natural
		Don River	31.6	1.0	4.5	modified
		Trent River	1,270	41.1	168.0	modified
		Sub Total	1,390	45.0	409.0	N/A
TOTAL	21,800		7,280	33.4	1090.	

* Lake Erie diversion via Welland Canal

TABLE 2: WATER QUALITY PARAMETERS MEASURED AT THE ENHANCED TRIBUTARY MONITORING STATIONS

NO3 F sol P/20

Tributary	Suspended Solids	Total Phosphorus	Filtered Reactive Phosphate-P	Nitrate-Nitrogen	Copper Cu	Lead Pb	Cadmium	Mercury Hg	PCB	PCP	2,4,5-T
Kaministiquia River	X	X	X	X	X	X	X	X	X	X	X
Little Pic River	X	X	X	X	X	X	X	X	X	X	X
Pic River	X	X	X	X	X	X	X	X	X	X	X
Black River	X	X	X	X	X	X	X	X	NS	NS	NS
Mississaugi River	X	X	X	X	X	X	X	X	NS	NS	NS
Spanish River	X	X	X	X	X	X	X	X	X	X	X
Saugeen River	*	X	X	X	X	X	X	X	NS	NS	NS
Sydenham River	X	X	X	X	X	X	X	X	NS	NS	NS
Thames River	X	X	X	X	X	X	X	X	X	X	X
Grand River	X	X	X	X	X	X	X	X	X	X	X
Welland River	X	X	X	X	X	X	X	X	X	X	X
Twelve Mile Creek	X	X	X	X	X	X	X	X	X	X	X
Humber River	X	X	X	X	X	X	X	X	X	X	X
Don River	X	X	X	X	X	X	X	X	X	X	X
Trent River	X	X	X	X	X	X	X	X	NS	NS	NS

X - sampled by the contract observers and MOE Regional staff
* - sampled by the Water Survey of Canada
NS - not sampled

2.0 PROGRAM STUDY APPROACH

2.1 Tributary Selection

Historically, total phosphorus loadings have been computed by the MOE for the IJC Water Quality Board for approximately 60 significant Great Lakes tributary streams. Figure 1 illustrates both the standard error of phosphorus loadings and their magnitude for these streams for the 1973-1978 period. From this group, 15 tributaries were selected for inclusion in the Enhanced Tributary Monitoring Program. Eleven tributaries with loadings of greater than 300 kilograms per day were selected on the basis of greatest magnitude (Figure 1). Four additional tributaries were selected from a group of 12 streams with loading rates in the 100 to 300 kilogram per day range. Selection of these four tributaries was governed primarily by the desire to attain a more uniform allocation of monitoring among the Great Lakes. The tributaries selected are listed in Table 1.

2.2 Water Quality

The water-quality parameters measured at each of the monitoring sites are listed in Table 2. Analyses of the water samples were conducted primarily at the MOE Central laboratory located in Toronto. Some trace elements and nutrient analyses from the Lake Superior basin, were conducted at the MOE Thunder Bay laboratory.

The water-quality data collected in this program are published with the data from the remainder of the Provincial Water Quality Network (PWQN) in the annual Water Quality Data Series (Volume XV, 1979 and Volume XVI, 1980 Water Quality Data, Ontario Lakes and Streams).

2.2.1 Sample Collection Methods

Local contract observers were hired to collect water-quality samples. The sampling apparatus, collection techniques, preservation and storage were consistent with those adopted for the PLUARG program (Onn, 1980). Specially prepared sample containers, chemical preservation and cold storage were used to inhibit chemical reactions and microbial activity.

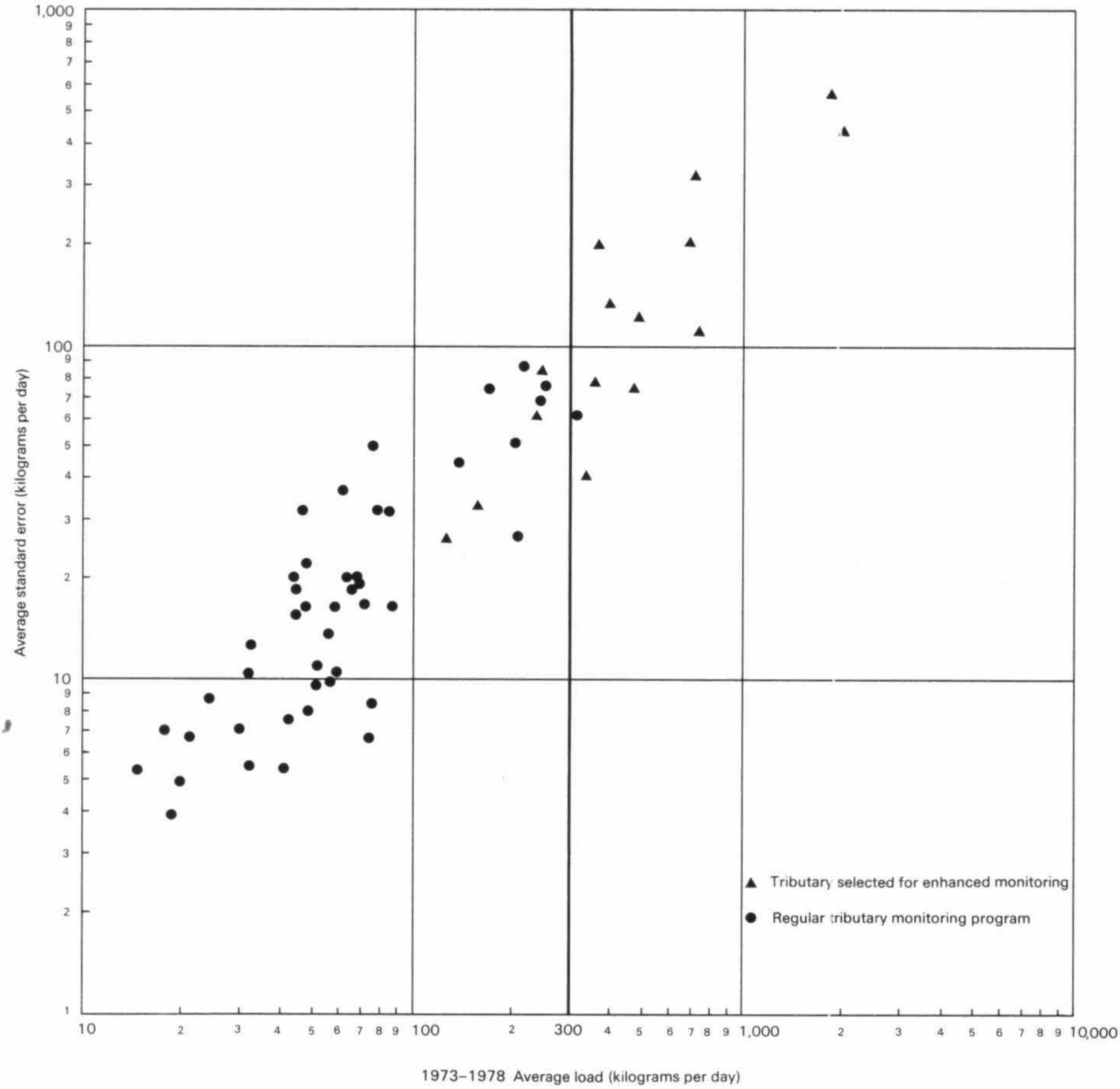


Figure 1. Variation of the historic phosphorus loading estimates (1973–1978) at the sixty Great Lakes significant tributary streams.

Representative samples were collected by depth-integration techniques. Samples were collected by raising and lowering the sample container at a constant velocity through one or more sampling verticals at each monitoring station. The number of sampling verticals varied at each monitoring site from one to three because of the seasonal variability in the magnitude of streamflow and the width of each tributary cross-section.

2.2.2 Sample Collection Frequency

To achieve an effective sampling frequency, the 15 tributaries were characterized through examination of their hydrographs into two basic categories, "natural" and "modified". The "natural" category exhibits flow patterns of a high spring runoff period followed by a recession to low summer flows (see figure 2a). Tributaries in the "modified" category exhibit patterns of flow resulting from the presence of major dams, diversions and/or urbanization (see figure 2b, 2c) which are distinctly different from those shown in the "natural" category described above.

Although the basic sample strategy was similar for all sites (i.e. frequent sample collection during high flow), two plans for sampling frequency were adopted. Sampling frequencies for the monitoring sites grouped within the "natural" category were keyed to three predetermined flow ranges; high-event flow, event flow and baseflow. Sampling frequencies for the monitoring sites within the "modified" category varied from once per week to once per day with emphasis directed towards periods when high flows were expected to recur. Annual sampling frequency for both types of hydrograph categories ranged from 60 to 110 samples.

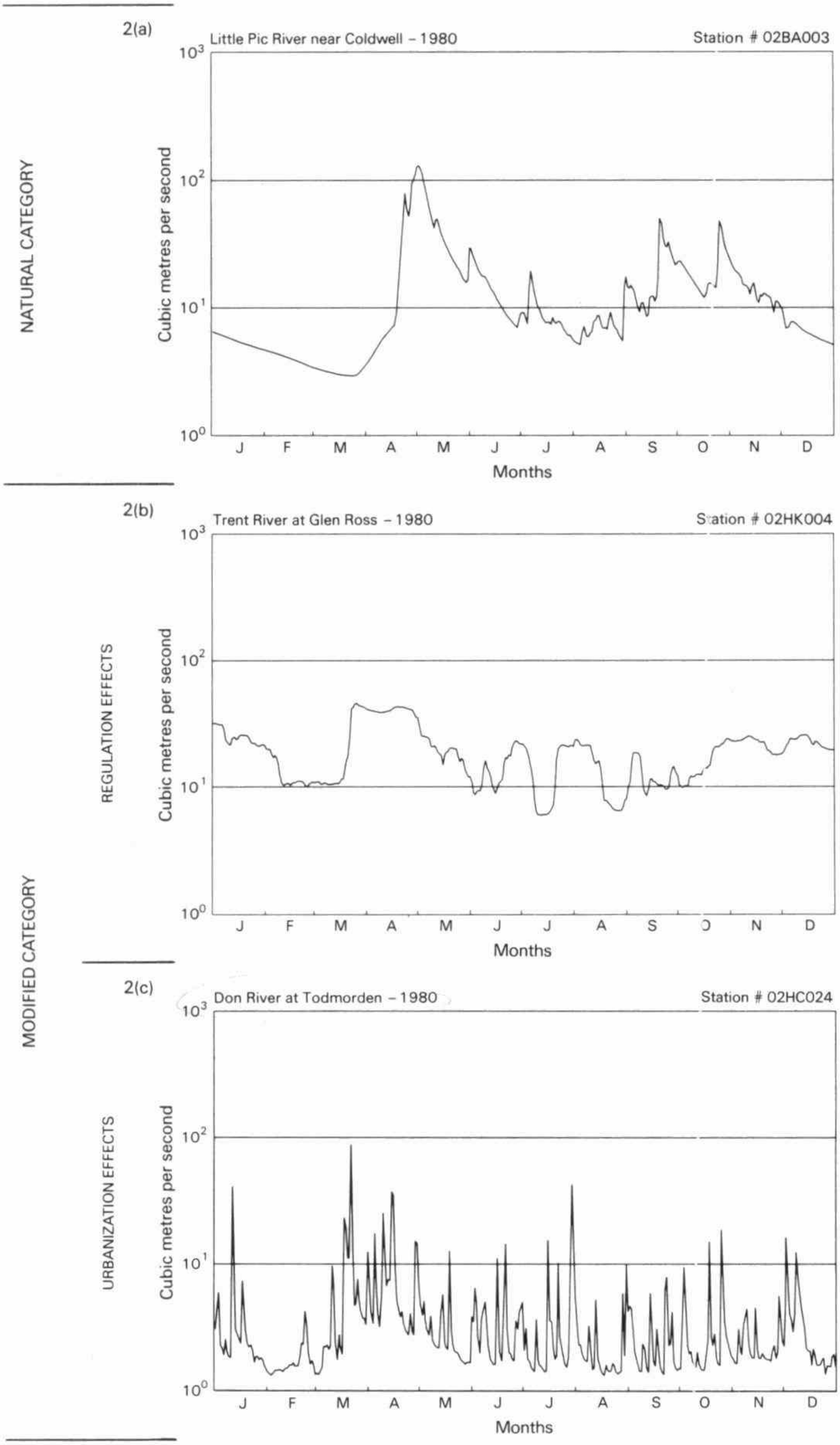


Figure 2. Streamflow hydrograph categories.

2.3 Water Quantity

Records of streamflow for this program were generally obtained from the Water Resources Branch of Environment Canada. Some additional records detailing discharge diversions from the Welland Canal to both the Welland River and Twelve Mile Creek were obtained from the Western Region Office, St. Lawrence Seaway Authority.

Where possible, water-quality sampling sites were located coincident with established Environment Canada streamflow gauges to facilitate the use of mean daily discharge records for the computation of load estimates. Additional records of discharge every hour were also obtained for major runoff events at these sites. These hourly discharges were used to aid in the definition of start and stop times for specific events when interpreting the data record.

In cases where no suitable streamflow gauges exist at sites, discharges for the watershed outlets were estimated by using data from (one or more) upstream gauges. This was accomplished by developing flow estimator equations based on drainage areas. For example, on the Sydenham River, water-quality sampling was carried out at Wallaceburg, downstream of the confluence of the north branch of the Sydenham River (Bear Creek) and the main stream. Gauges are located about 20 kilometres upstream of Wallaceburg as follows:

Station 02GG004 - Bear Creek above Wilkesport - 609 km^2
Station 02GG007 - Sydenham River near Dresden - 1240 km^2

Estimates of mean daily discharge at the Wallaceburg site, with a total watershed area of 3200 km^2, were derived with the equation:

$$\text{Total flow} = \text{flow at 02GG004} \times 1.9 + \text{flow at 02GG007} \times 1.6$$

To avoid problems with lag time, no attempt was made to provide estimates of discharge every hour for tributaries requiring the flow estimator equation.

2.4 Loading Computation Technique

The objective of the loading computation is to determine the mean of the load population (L) for the required time interval.

All tributary loading computations included the use of a ratio estimator attributed to E.M.L. Beale and advocated for use since 1976 by the International Joint Commission (IJC). This estimator is discussed in detail in the IJC Quality Control Handbook for Pilot Watershed Studies (International Reference Group on Great Lakes Pollution from Land Use Activities, 1975, Section 7.5). The ratio estimator involves the relationship between two related populations, in this case flow and load. The flow population is used to improve the estimate of the load by assuming that:

a) flows are monitored continuously and the mean flow (Q) may be determined;

b) discrete observations are available on the load population (l) where $l_i = c_i q_i$ for l_i = load, c_i = concentration, and q_i = flow of sample;

c) the distributions of the flows and concentrations are approximately normal.

Use of the ratio estimator assumes that the populations of flows and concentrations are approximately normally distributed; however, the annual populations are most often highly skewed. Flows may vary over 2 to 3 orders of magnitude while concentrations of suspended solids can vary 3 to 4 orders of magnitude. The greatest variations are observed during rainfall-runoff events which, although they occupy a relatively small portion of the year on a time basis, contribute significantly to the total annual runoff and load. An effective means of treating such populations is to divide them into relatively homogeneous strata within which the subpopulations more closely approach normality. Within strata, the ratio estimator is used to estimate the load and variance. Estimates for individual strata are then combined arithmetically to produce a pooled estimate of load for the annual period.

Analyses were performed with a modified version of a FORTRAN program originally developed by PLUARG investigators. Stratification of the record was a subjective procedure based on consideration of both the annual flow record and the sample concentration data. Flow events were identified and the behaviour of concentrations with respect to flows noted. The concentrations for most parameters were found to hold a generally positive relationship with flow (i.e. increasing during flow events in proportion to the magnitude of the event) allowing definition of concentration ranges for various ranges of flow. Strata boundaries were then defined by assigning flow cut-off values. For example, at the mouth of the Grand River, suspended-solids concentrations for the springmelt period ranged from 230 to 784 mg/L with a mean daily flow of 504 m^3/s. While data for all parameters were reviewed, experience showed that focusing on the most sensitive parameter, suspended solids, led to a stratification scheme suitable for all other parameters without any great loss in precision.

For the tributaries with "natural" flow conditions, a four-strata approach as follows was generally used:

stratum 1 - event flow
stratum 2 - high-event flow
stratum 3 - cold water/winter baseflow
stratum 4 - warm water/summer baseflow

For the tributaries with heavily regulated flows (Kam, Mississaugi, Spanish, Welland, and Trent Rivers and Twelve Mile Creek), a two-strata approach was generally used. The spring period was placed in stratum 2 and the remainder of the year in stratum 1.

3.0 DATA INTERPRETATION AND DISCUSSION

3.1 Water Quality Measurements

As previously mentioned, water-quality samples collected in the ETM program were analyzed at the Ministry of the Environment's laboratories located in Toronto and Thunder Bay. Water-quality samples collected from Lake Superior tributaries were analyzed in Thunder Bay with the exception of those samples intended for PCB, PCP and 2,4,5-T analyses which were forwarded to the Toronto laboratory. All other water-quality samples were delivered to and analyzed at the Toronto laboratory.

The laboratory measurements (i.e. pollutant concentrations) of water-quality samples collected during the 1980 water-year (October 1979 to September 1980) are illustrated for suspended solids; nitrate-nitrogen; total phosphorus; reactive phosphate; cadmium; copper; lead; mercury; PCB; and PCP respectively. The concentration ranges (i.e. minimum to maximum concentration) for each water-quality parameter are denoted with a solid vertical line on logarithmic scale, for each of the tributary outlet monitoring stations. An arrow appears at the lower end of the vertical line where one or more of the measured concentrations is less than the analytical detection limit reported by the laboratory. The range of analytical detection limit concentrations is shown for water-quality parameters since detection limits are variable from day-to-day and are not consistent between laboratories. The number of samples and, where applicable, the percentage of samples exceeding the Provincial Water Quality Objective (PWQO) is also shown. The flow-weighted mean concentration is marked on the vertical line with the symbol "X" or where one or more analytical results were found to be less than the detection limit, the flow-weighted mean concentration is marked on the vertical line with the symbol "<". Where sufficient data exist, the standard error is marked on the vertical line with horizontal bars, above and below the flow-weighted mean concentration.

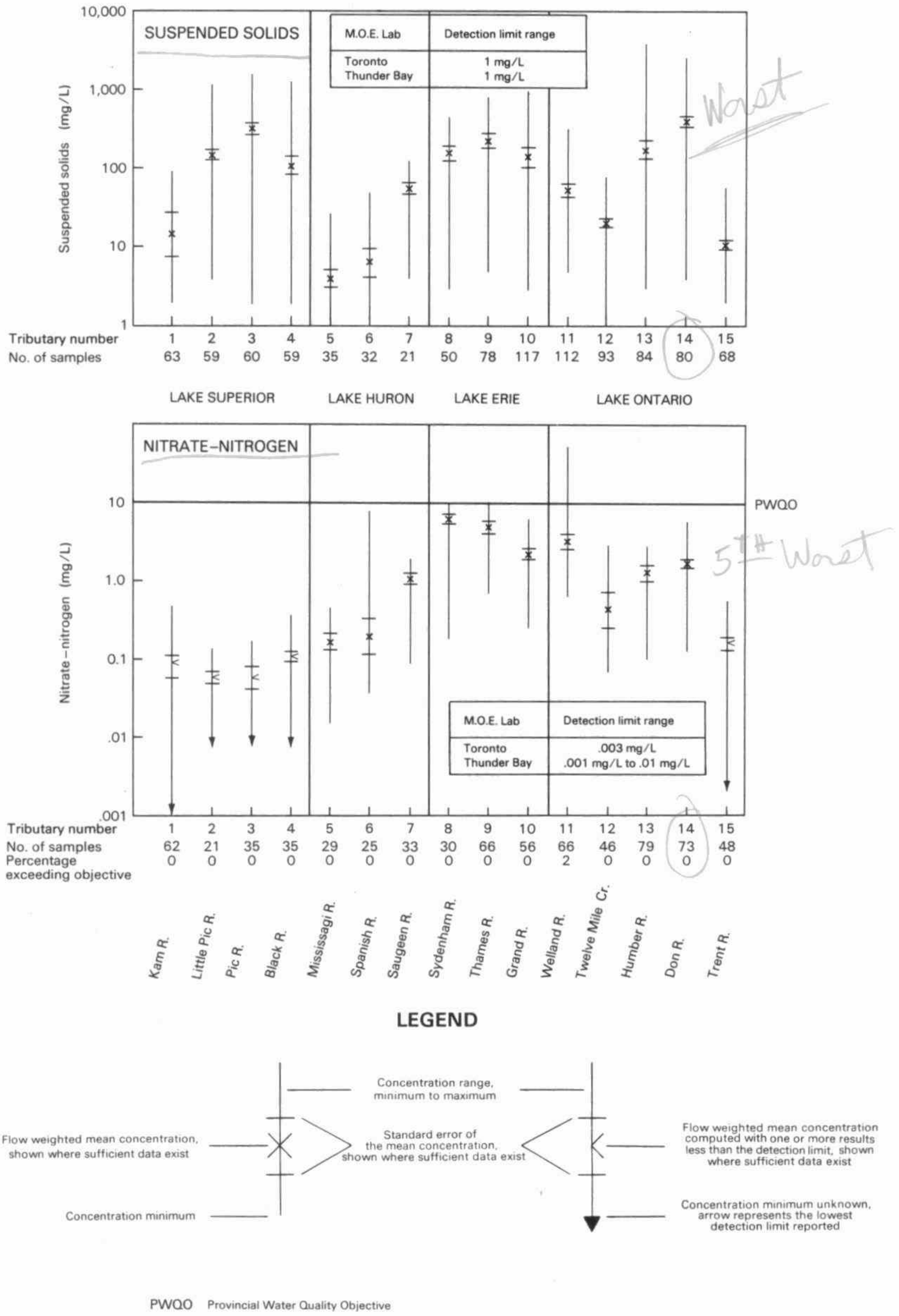


Figure 3a. 1980 water-year, tributary concentration measurements: suspended solids, nitrate-nitrogen.

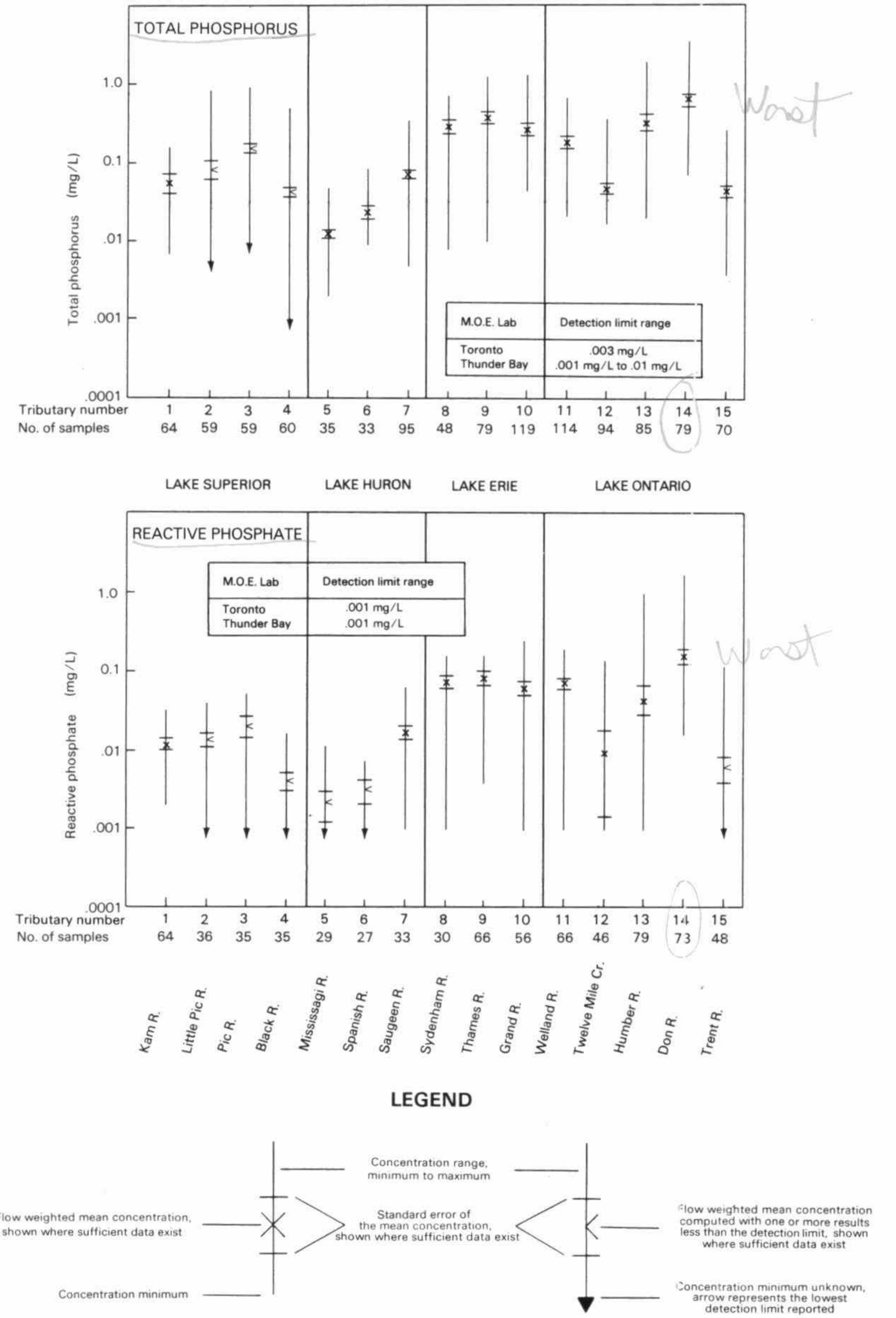
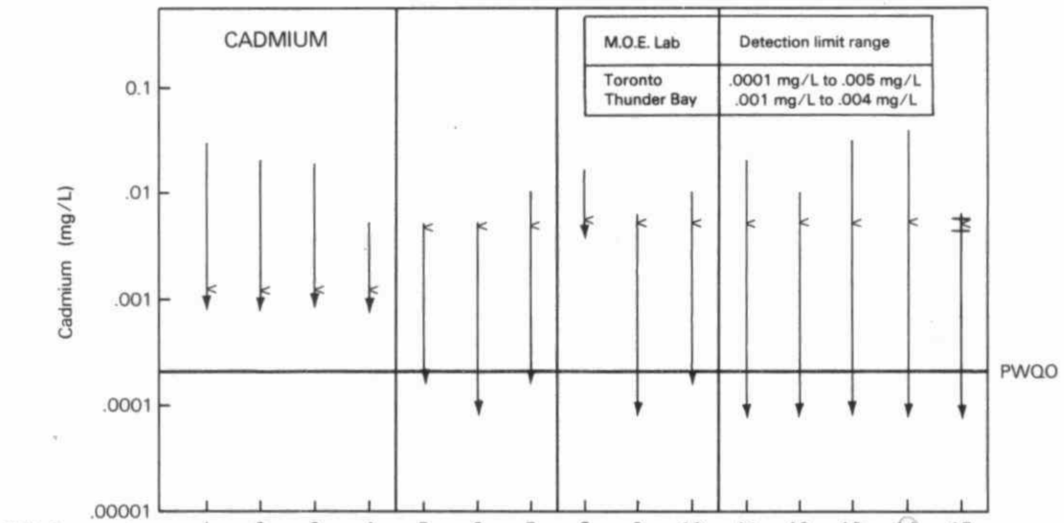
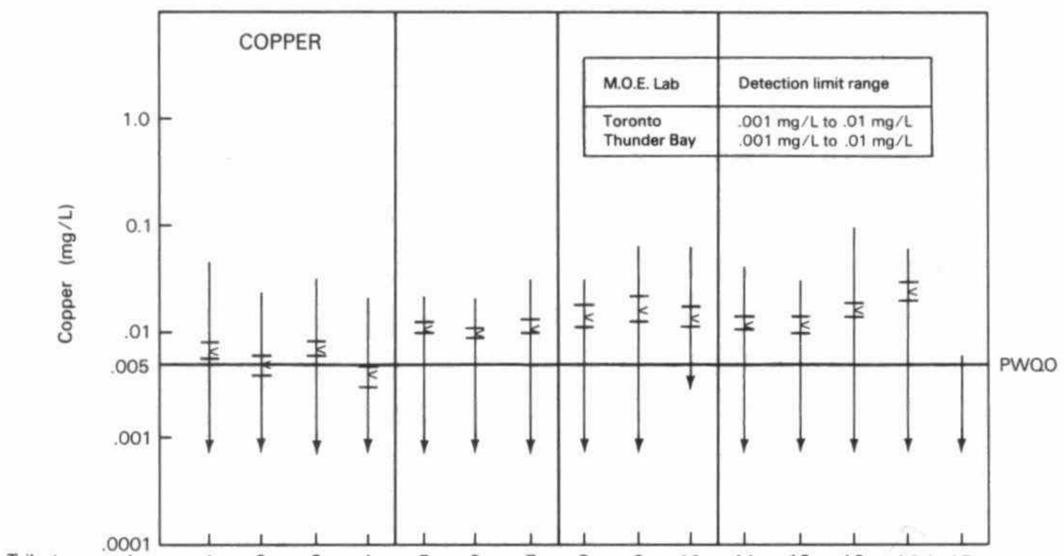


Figure 3b. 1980 water-year, tributary concentration measurements: total phosphorus, reactive phosphate.



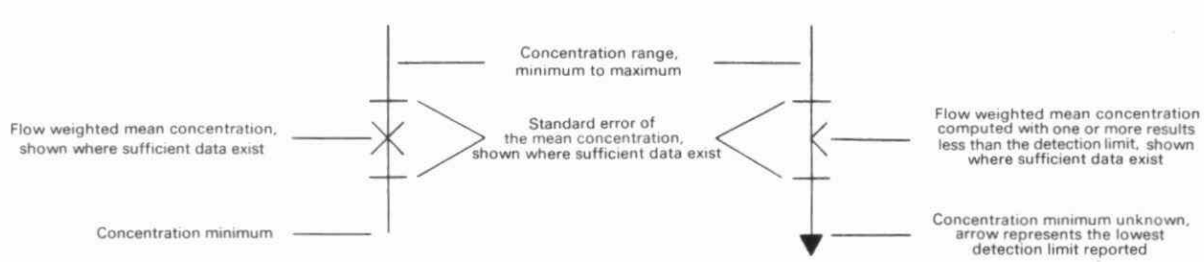
Tributary number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
No. of samples	60	59	59	59	32	30	96	37	63	101	97	74	78	75	63
Percentage exceeding objective	≥47	≥63	≥64	≥56	≥3	≥3	≥4	≥8	≥3	≥6	≥4	≥9	≥55	≥9	≥3

LAKE SUPERIOR LAKE HURON LAKE ERIE LAKE ONTARIO



Tributary number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
No. of samples	60	37	37	36	25	26	36	30	50	48	62	42	75	72	41
Percentage exceeding objective	≥50	≥46	≥54	≥31	≥8	≥8	≥11	≥27	≥34	≥33	≥27	≥26	≥33	≥57	≥10
	Kam R.	Little Pic R.	Pic R.	Black R.	Mississagi R.	Spanish R.	Saugeen R.	Sydenham R.	Thames R.	Grand R.	Welland R.	Twelve Mile Cr.	Humber R.	Don R.	Trent R.

LEGEND



PWQO Provincial Water Quality Objective

≥ Greater than or equal to; the "percentage exceeding objective" is qualified with this symbol where one or more analytical results are reported to be less than a detection limit which exceeds the PWQO (ie. these qualified analytical results may not exceed the PWQO).

Figure 3c. 1980 water-year, tributary concentration measurements: cadmium, copper.

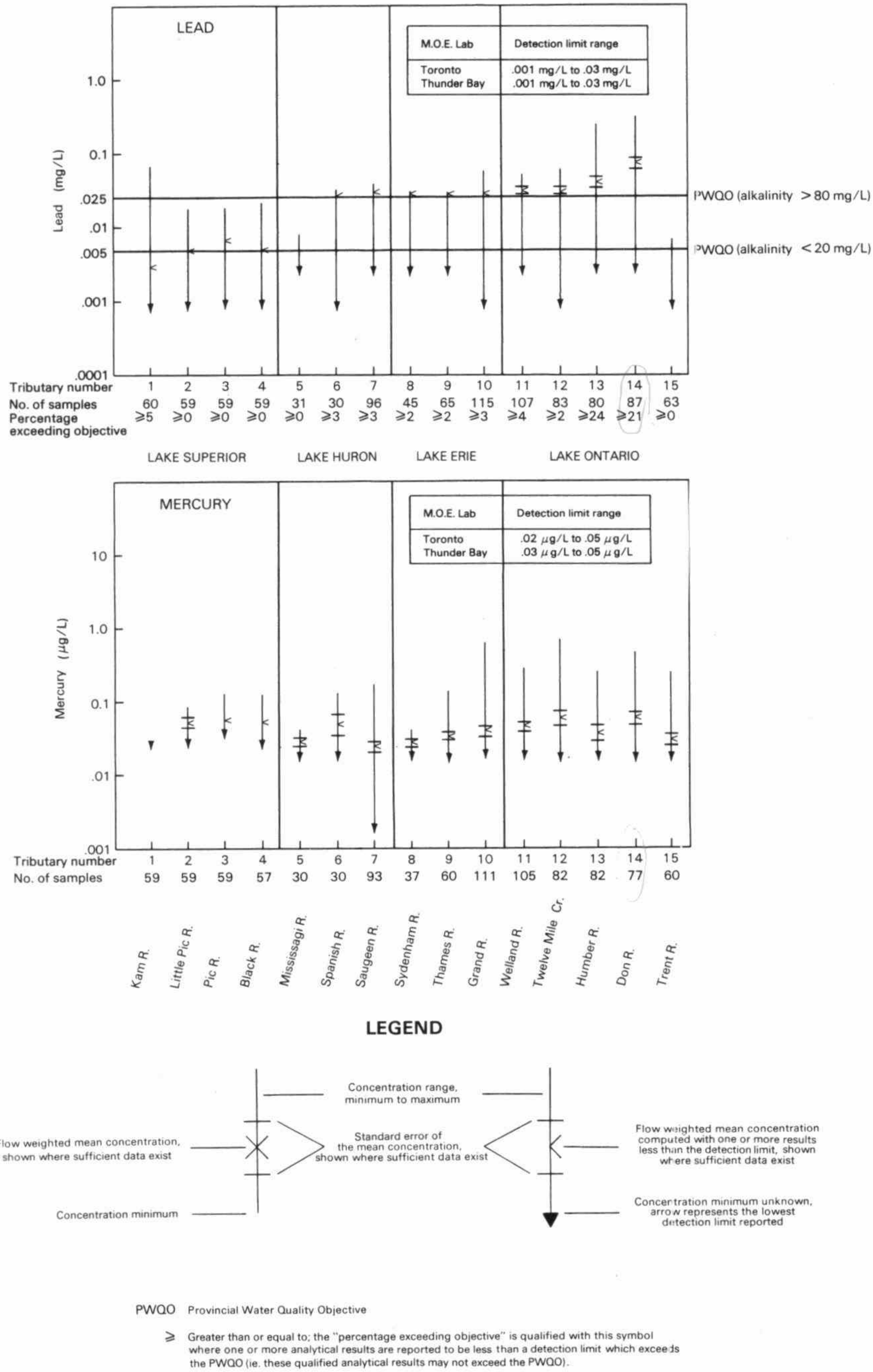
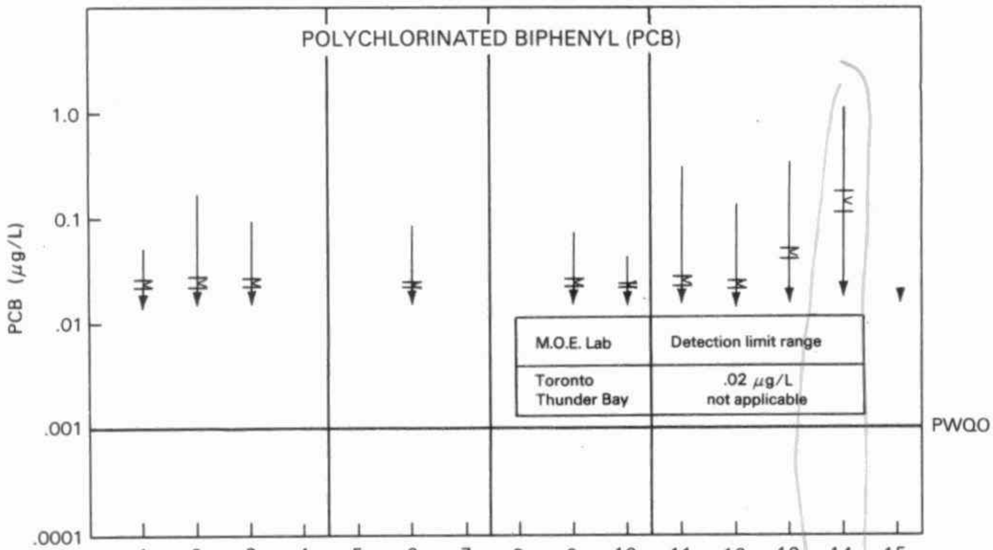
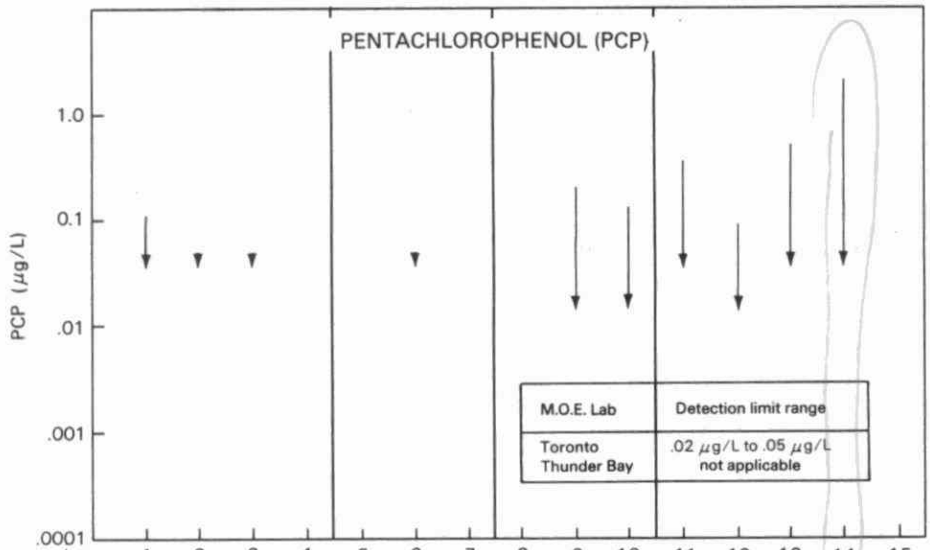


Figure 3d. 1980 water-year, tributary concentration measurements: lead, mercury.



Tributary number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
No. of samples	49	47	52	0	0	29	0	0	59	92	103	65	75	74	5
Percentage exceeding objective	≥12	≥4	≥10			≥10			≥7	≥7	≥15	≥12	≥36	≥42	ND

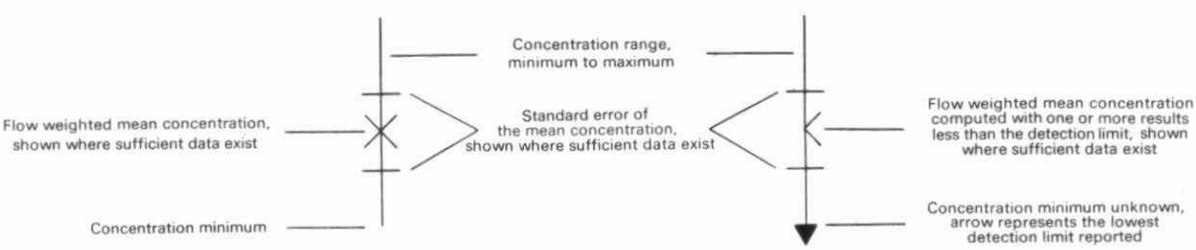
LAKE SUPERIOR — LAKE HURON — LAKE ERIE — LAKE ONTARIO



Do IC sediment this parameter done

Tributary number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
No. of samples	16	7	6	0	0	3	0	0	3	7	27	12	33	31	0
Remark		ND	ND			ND									
	Kam R.	Little Pic R.	Pic R.	Black R.	Mississagi R.	Spanish R.	Saugeen R.	Sydenham R.	Thames R.	Grand R.	Welland R.	Twelve Mile Cr.	Humber R.	Don R.	Trent R.

LEGEND



PWQO Provincial Water Quality Objective

ND Not detected

≥ Greater than or equal to; the "percentage exceeding objective" is qualified with this symbol where one or more analytical results are reported to be less than a detection limit which exceeds the PWQO (ie. these qualified analytical results may not exceed the PWQO).

Figure 3e. 1980 water-year, tributary concentration measurements: PCB, PCP.

As shown by the comparsions of flow-weighted mean concentration and concentration range (i.e. minimum to maximum concentration), the highest values generally occur in monitored tributaries of lakes Erie and Ontario for the variables suspended solids, nitrate-nitrogen, total phosphorus, reactive phosphate, copper, lead and mercury. Flow-weighted mean concentrations from these tributaries were used to identify exceedences of the Provincial Water Quality Objectives.* The flow-weighted mean concentration is in violation for copper at all tributaries except at the Little Pic and Black rivers; and for lead at all tributaries except at the Pic, Little Pic, Black and Kaministikwia. The analytical detection limit for cadmium is variable (.0001 mg/L to .005 mg/L), both "less than" and "greater than" the Provincial Water Quality Objective (.0002 mg/L) because the analytical methodology was modified during the study period. The analytical detection limit for PCB (.02 ug/L) is significantly higher than the Provincial Water Quality Objective (.001 ug/L) and PCBs were detected on one or more occasions at all of the tributaries that were sampled for PCBs (i.e. Black, Mississagi and Sydenham were not sampled for PCB). PCP and 2,4,5-T are substances with undefined tolerance limits (1978, Ministry of Environment) and both compounds were detected on one or more occasions at all tributaries that were measured (Black, Mississagi, Saugeen, Sydenham, Thames and Trent were not sampled for these parameters).

1980 report

* Current scientific evidence is insufficient to develop a firm Provincial Water Quality Objective for total phosphorus. However, in place of a firm objective, the total phosphorus concentration of 30 μg/L is considered as a general guideline for rivers and streams.

3.2 Multi-Strata Load Estimates

Annual load estimates derived from the multi-strata computation technique for the variables suspended solids, total phosphorus, reactive phosphate, nitrate-nitrogen, cadmium, copper, lead, and mercury are provided on Table 3. The table presents mean daily loading in kilograms per day, the standard error of the mean and the number of samples used to derive the load.

Concentrations found to be less than the analytical detection limit were commonly measured for the variables cadmium, copper, lead and mercury. When this was the case, the detection limit value was used for computation and the resulting load estimates are assumed to overestimate the true load. Load estimates computed in this manner have been flagged with a "less than" (L) remark.

Figures 4a and 4b are graphic illustrations of the loading estimates for the eight water-quality variables reported in Table 3. The variables have been separated into two distinct groups namely, nutrients (figure 4a) and trace elements (figure 4b).

Suspended-solids analyses provide gross measurements of the amounts of particulate matter found in the water. They are of interest, as suspended solids serve as a transporting agent for a host of other parameters including some important forms of the nutrients (phosphorus and nitrogen) and many of the trace elements, all of which tend to exhibit similar patterns of increasing concentration with increasing flow. Examination of the distribution of suspended-solids loading estimates (figure 4a) shows 81% of the enhanced tributary load is delivered by four tributaries - the Sydenham, Thames, Grand and Pic rivers. Together, the Sydenham, Thames and Grand rivers, all tributary to Lake Erie, deliver 45% of the total enhanced tributary, suspended-solids load. While solids enter watercourses from many sources, including sewage treatment plants and urban runoff, the intensive agricultural activity in southwestern Ontario is likely the cause of the high component in the Lake Erie basin. The Pic River in the Lake Superior basin provides the greatest individual solids component with 25% of the

TABLE 3: 1980 WATER YEAR, TRIBUTARY LOAD ESTIMATES

Key: N X (Y) — N: Number of Samples; X: Mean Daily Loading (kilograms/day); Y: Standard Error of the Mean

L: Less Than -: Not Sampled

Parameters / Tributaries	N	Suspended Solids	N	Nitrate Nitrogen	N	Total Phosphorus	N	Reactive Phosphate	N	Cadmium	N	Copper	N	Lead	N	Mercury	N	PCB
Kaministikwia River	62	61,900 (10,000)	61	336 (54.5)	63	208 (18.3)	63	45.6 (3.06)	55	4.00 (0.13)	55	27.6 (3.88)	57	11.1 (1.08)	56	0.190L (0.000)	47	0.083L (.003L)
Little Pic River	58	217,000 (16,700)	21	81.8 (6.58)	58	120 (11.6)	35	19.6 (1.76)	49	1.56 (0.07)	31	7.48 (0.90)	54	7.43 (0.66)	54	0.072L (0.000)	46	0.033L (.004L)
Pic River	60	1,400,000 (116,000)	35	261 (32.7)	59	648 (49.1)	35	88.5 (10.9)	49	5.46 (0.25)	30	32.0 (2.78)	54	31.6 (2.94)	53	0.219L (0.000)	51	0.098L (.007L)
Black River	58	323,000 (35,000)	34	318 (19.4)	59	123 (10.0)	34	11.9 (0.94)	48	3.30 (0.18)	29	13.0 (1.25)	52	15.7 (1.63)	49	0.147L (0.001L)	-	-
Mississagi River	30	44,200 (5310)	25	1920 (250)	31	131 (12.5)	25	21.0 (4.24)	22	56.5L (0.00)	19	120L (5.79L)	21	339L (0.00)	20	0.300L (0.019L)	-	-
Spanish River	32	99,000 (18,500)	24	2390 (402)	33	338 (32.6)	27	37.7 (5.64)	23	72.7L (0.00)	22	147L (6.98L)	24	426L (9.64L)	22	0.534L (0.119L)	29	0.311L (.016L)
Saugeen River	21	212,000 (12,300)	33	5880 (422)	96	390 (19.4)	33	90.2 (8.22)	84	27.5L (0.22L)	32	60.1L (5.88L)	87	163L (0.77L)	85	0.129L (0.011L)	-	-
Sydenham River	49	340,000 (33,000)	29	13,600 (487)	47	626 (45.3)	29	175 (10.0)	37	11.3L (0.12L)	27	31.8L (3.04L)	42	66.7L (0.00)	37	0.047L (.001L)	-	-
Thames River	76	1,200,000 (104,000)	64	29,100 (1360)	77	2190 (175)	64	486 (35.1)	51	29.6L (0.10L)	39	102L (13.6L)	52	177L (0.00)	48	0.187L (0.018L)	58	0.135L (.012L)
Grand River	114	938,000 (154,000)	56	16,000 (696)	117	1890 (216)	56	411 (28.2)	95	34.6L (0.77L)	42	93.2L (6.93L)	102	202L (1.45L)	95	0.19L (0.01L)	111	0.135L (.001L)
Welland River	103	122,000 (17,000)	63	7300 (728)	105	468 (36.0)	63	174 (12.4)	80	12.9L (0.45L)	51	28.2L (1.72L)	87	73.2L (0.88L)	84	0.081L (0.011L)	93	0.053L (.002L)
Twelve Mile	88	361,000 (23,000)	43	6610 (1280)	89	851 (48.4)	43	93.1 (12.3)	64	93.6L (3.00L)	36	202L (13.2L)	70	528L (8.78L)	70	0.826L (0.205L)	63	0.369L (.012L)
Humber River	46	134,000 (13,100)	44	922 (91.1)	47	254 (33.3)	44	32.3 (5.85)	38	3.76L (0.08L)	35	11.9L (0.54L)	38	30.8L (2.80L)	38	0.025L (0.002L)	39	0.032L (.006L)
Don River	62	152,400 (5870)	58	632 (23.5)	61	256 (14.4)	58	60.2 (6.19)	51	2.11L (0.12L)	49	9.20L (0.70L)	51	29.3L (2.25L)	51	0.022L (0.001L)	53	0.049L (.009L)
Trent River	65	138,000 (13,300)	44	2280 (179)	66	535 (22.9)	44	61.8 (7.6)	50	72.9L (0.36L)	30	150L (4.53L)	50	435L (0.00)	48	0.413L (0.040L)	-	-

monitored suspended-solids load for the 15 tributaries. Extensive deposits of lacustrine clay, silt and fine sand within the Pic watershed probably contribute to the unusually high solids load.

The variable of major interest with respect to loadings to the Great Lakes, total phosphorus, exhibits the greatest loading rates in the Lake Erie tributaries (figure 4a). Together, the Sydenham, Thames and Grand rivers deliver 52% of the total phosphorus load for the streams monitored in this enhanced program. This large component can probably be attributed to the intensive agricultural activity in these basins. Ranking next in size, Twelve Mile Creek and the Welland River deliver an additional 15% of the load. A major component of the flow here is comprised of Lake Erie waters diverted to these watercourses by way of the Welland Canal (Table 1). The higher loading rates of the Welland River and Twelve Mile Creek are a reflection of the large water diversions from Lake Erie as well as higher phosphorus concentrations in the Welland River (figure 3b). The Pic River of Lake Superior ranks next, delivering approximately 7% of the total phosphorus load monitored in the enhanced tributaries. High phosphorus loads here are attributed to high sediment loads probably reflecting natural soil phosphorus losses.

Reactive phosphate is primarily the dissolved form of inorganic phosphorus and is generally considered to be readily available for aquatic plant growth. The distribution of load estimates for this variable (figure 4a) is very similar to that shown by total phosphorus. The three streams tributary to Lake Erie are of major importance delivering 59% of the reactive phosphate load monitored from the 15 tributaries, followed by the Welland River and Twelve Mile Creek with an additional 15%. The remaining 26% is more or less uniformly distributed among the other 10 tributaries.

Nitrate-nitrogen is the end product of the stabilization of organic nitrogen. Elevated levels of nitrate are usually found in polluted waters that have undergone some degree of self-purification and also occur in watercourses draining fertilized agricultural areas. Examination of the distribution of filtered nitrate loading estimates (figure 4a) shows 90% of the enhanced tributary load is

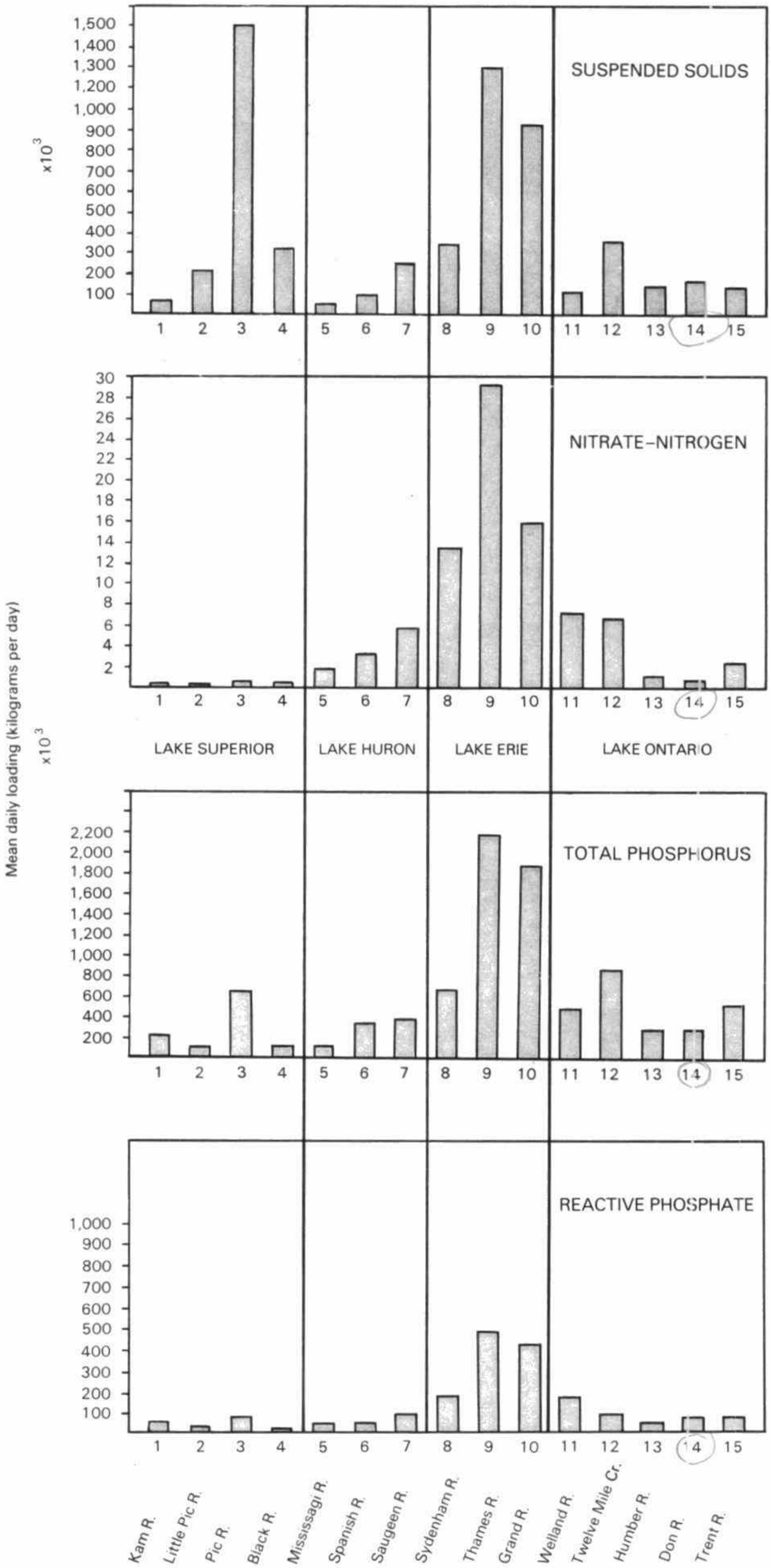


Figure 4a. 1980 water-year, tributary loading estimates: suspended solids, nitrate-nitrogen, total phosphorus, reactive phosphate.

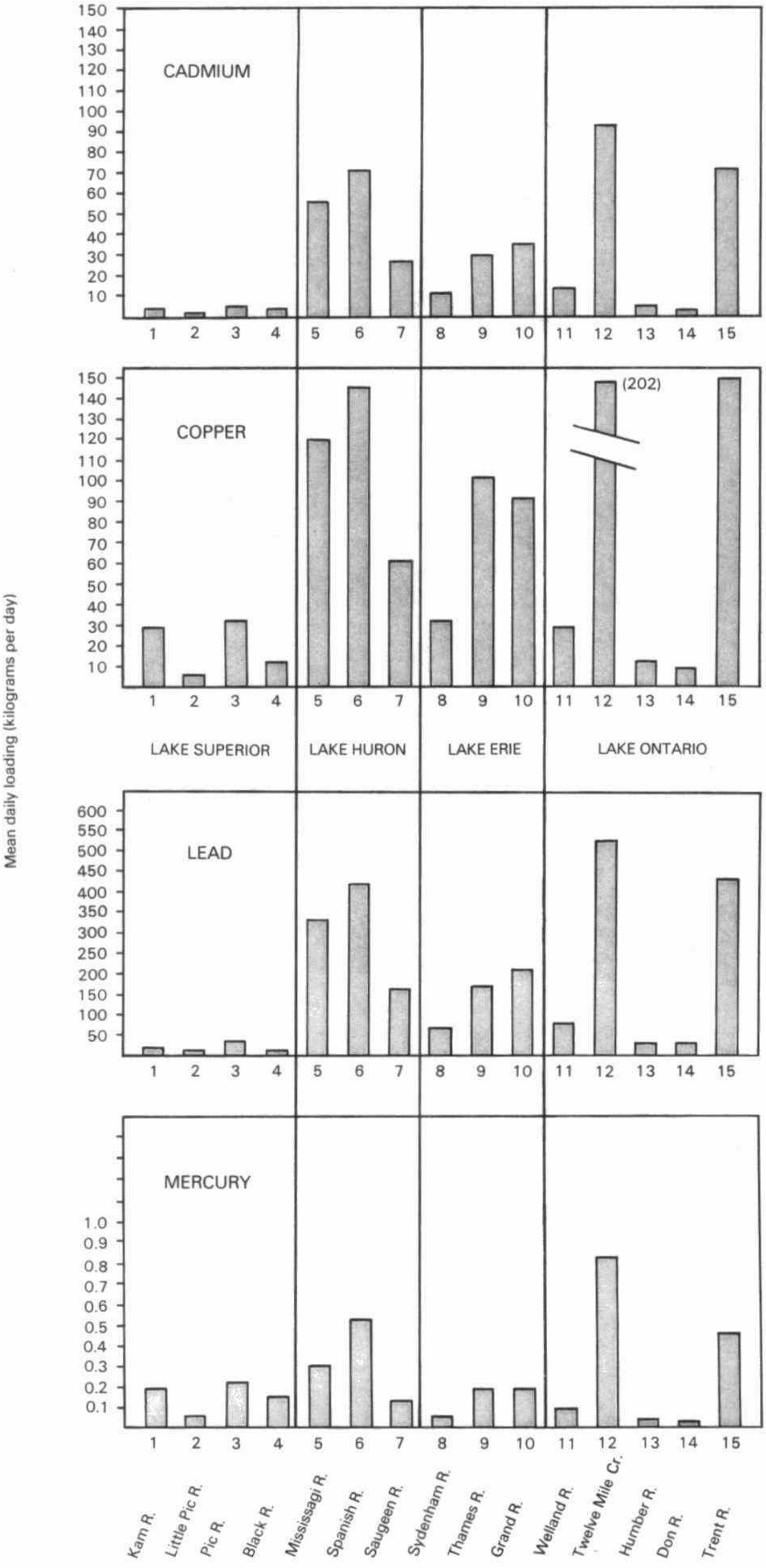


Figure 4b. 1980 water-year, tributary loading estimates: cadmium, copper, lead, mercury.

delivered by six tributaries - the Saugeen, Sydenham, Thames, Grand and Welland rivers and Twelve Mile Creek. The intensive agricultural activity in southwestern Ontario is likely the source. By contrast, the four Lake Superior tributaries deliver only 1% of the nitrate-nitrogen load.

The distribution of loading estimates for the four trace element variables, cadmium, copper, lead and mercury, show that 60 to 70% of the load is consistently delivered by four tributaries, the Mississagi, Spanish and Trent rivers and Twelve Mile Creek (figure 4b). These four tributaries have an order of magnitude higher flows than the remaining 11 tributaries and consequently the loads reflect the high volume of water transported past their respective outlets.

3.3 Improved Precision of Load Estimates

A major goal of the Enhanced Tributary Monitoring Program (ETMP) is to improve the precision of the load estimates through additional water-quality sampling to allow the application of a more precise, stratified, loading computation technique. Historically, total phosphorus loading estimates have been derived from a limited data base of 12 to 14 water-quality samples per year. While the historic computations have included the use of a ratio estimator, the number of water-quality samples has generally been insufficient to allow stratification to reduce the bias from the skewed distribution of the data.

In order to evaluate the improvement in precision resulting from the current multi-strata load estimates, single stratum load estimates were computed for each tributary by selecting 14 samples from the ETMP data base (i.e. two samples per month for two high-flow months and one sample per month for the remainder of the year) and the results compared. This comparison was undertaken for total phosphorus, a particulate related parameter, and nitrate-nitrogen, a soluble parameter, at each sampling. For certain variables (e.g. PCB and cadmium), the loading precision will not improve until laboratory detection limits are consistently lower.

Comparison of the current loading estimates computed by multi-strata technique with those resulting from a 14-sample, single-stratum computation is presented in Table 4. The table presents the mean daily loading estimate in kilograms, the standard error expressed as a percentage of the mean, and the number of samples used to derive the load estimate. For total phosphorus, the mean standard error for the 15 tributaries improved from 36.2% for the single stratum, 14-sample computations to 8.09% for the multi-strata estimates. For nitrate-nitrogen, similarly, values improved from 23.2% to 9.55%.

TABLE 4: COMPARISON OF MULTI-STRATA AND SINGLE-STRATUM LOAD ESTIMATES: TOTAL PHOSPHORUS AND NITRATE-NITROGEN

Parameters / Tributaries	N	Total Phosphorus Multi-Strata	N	Total Phosphorus Single-Stratum	N	Nitrate-Nitrogen Multi-Strata	N	Nitrate-Nitrogen Single-Stratum
Kam River	62	208	14	302	61	336	14	558
SE (%)		(8.80%)		(27.5%)		(16.2%)		(35.5%)
Little Pic R.	58	120	14	270	21	81.8	12	125
SE		(9.67%)		(51.1%)		(8.04%)		(41.3%)
Pic River	59	648	14	1900	35	261	14	435
SE		(7.58%)		(62.6%)		(12.5%)		(41.8%)
Black River	59	123	14	304	34	318	14	440
SE		(8.13%)		(52.0%)		(6.10%)		(31.1%)
Mississagi R.	31	131	13	150	25	1920	13	1950
SE		(9.54%)		(13.3%)		(13.0%)		(18.6%)
Spanish River	33	338	13	354	24	2390	13	3180
SE		(9.64%)		(17.0%)		(16.8%)		(33.3%)
Saugeen River	96	390	14	816	33	5880	14	6270
SE		(4.97%)		(62.3%)		(7.18%)		(13.7%)
Sydenham River	47	626	14	844	29	13,600	12	14,500
SE		(7.24%)		(50.6%)		(3.53%)		(20.3%)
Thames River	77	2190	14	3200	64	29,100	14	27,900
SE		(7.99%)		(42.8%)		(4.67%)		(12.7%)
Grand River	117	1890	14	1980	56	16,000	13	17,200
SE		(11.4%)		(36.5%)		(4.35%)		(13.4%)
Welland River	105	468	14	414	63	7300	14	5190
SE		(7.69%)		(20.2%)		(9.97%)		(16.6%)
Twelve Mile	89	851	14	1080	43	6610	14	5250
SE		(5.69%)		(29.6%)		(19.4%)		(17.3%)
Humber River	47	254	14	128	44	922	14	936
SE		(13.1%)		(24.9%)		(9.88%)		(14.7%)
Don River	61	256	14	190	58	632	14	760
SE		(5.63%)		(14.6%)		(3.72%)		(5.45%)
Trent River	66	535	14	768	44	2280	12	4130
SE		(4.28%)		(37.9%)		(7.85%)		(31.5%)
Mean Std. Error		8.09%		36.2%		9.55%		23.2%
Std. Deviation		2.40%		16.8%		5.06%		11.5%

3.4 Sample Strategy Analysis

The required number of samples for various levels of precision can be determined theoretically where a prior data base exists and strata boundaries have been defined. After satisfactorily completing the multi-strata load estimates, a sampling strategy analysis was conducted using an option of the FORTRAN program.

Assuming sufficient stratification, the number of samples theoretically required to achieve various levels of precision for total phosphorus for all 15 tributaries are presented in Figure 5a. For example, to achieve ±20% precision for total phosphorus sampling requirements across the various tributaries range from 10 (Trent River) to 55 (Humber River) samples. To improve the precision to ±10%, the number of samples theoretically required increases to 44 and 210 samples. It is clearly evident that a considerable expenditure of resources (i.e. additional samples for analysis) would be necessary to improve the precision from ±20% to ±10%.

Figure 5b presents the same sampling strategy analysis for the water-quality parameter nitrate-nitrogen. Here, for ±20% precision, sampling requirements across the tributaries range from 3 (Sydenham River) to 150 (Twelve Mile Creek) samples. To improve the precision to ±10% the number of samples increases to 12 and 600, respectively, again a significant increase. Although not shown, similar results could be expected for the remainder of the water-quality variables.

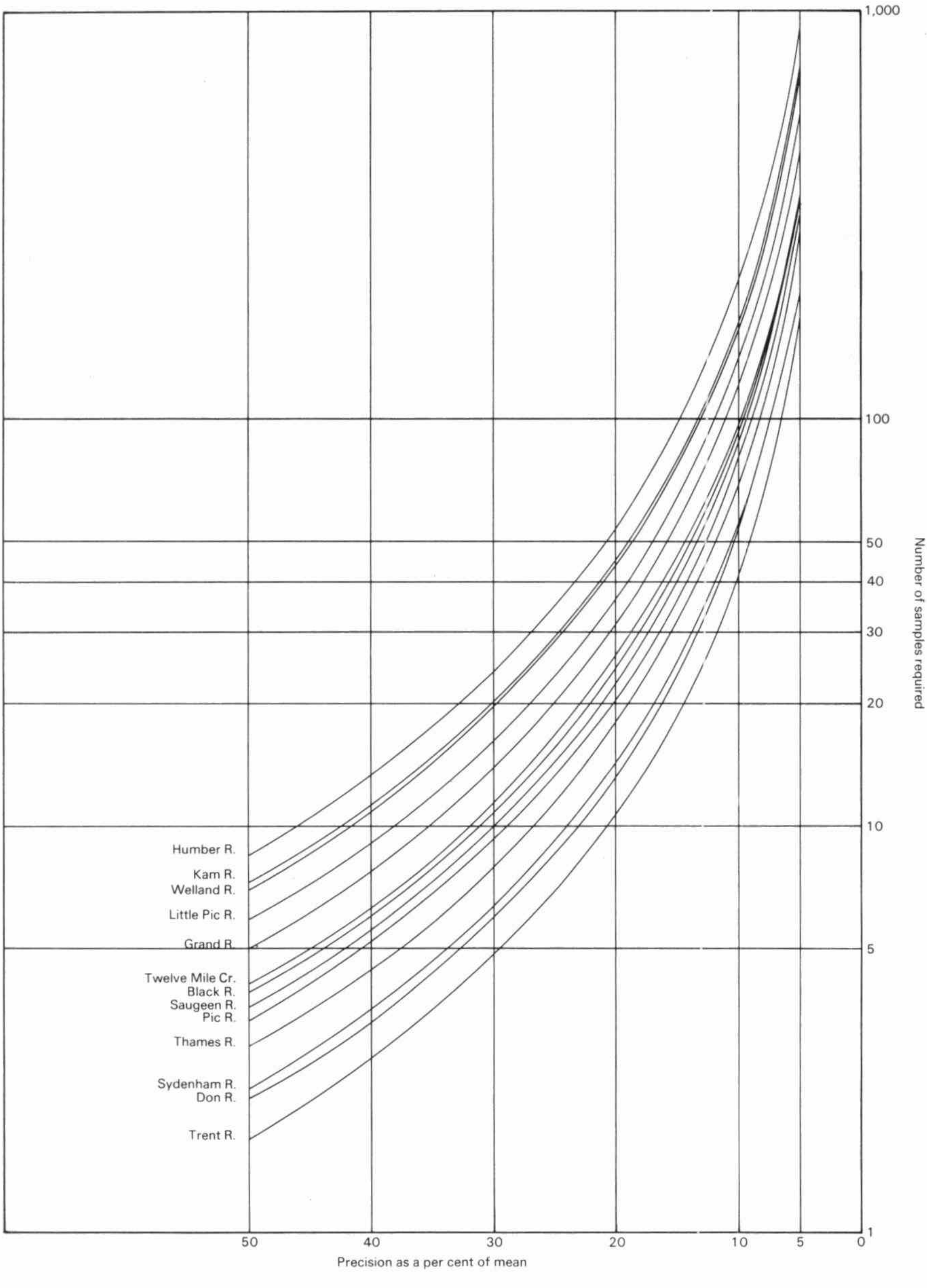


Figure 5a. Annual sampling frequency requirements to achieve varying levels of loading precision: total phosphorus.

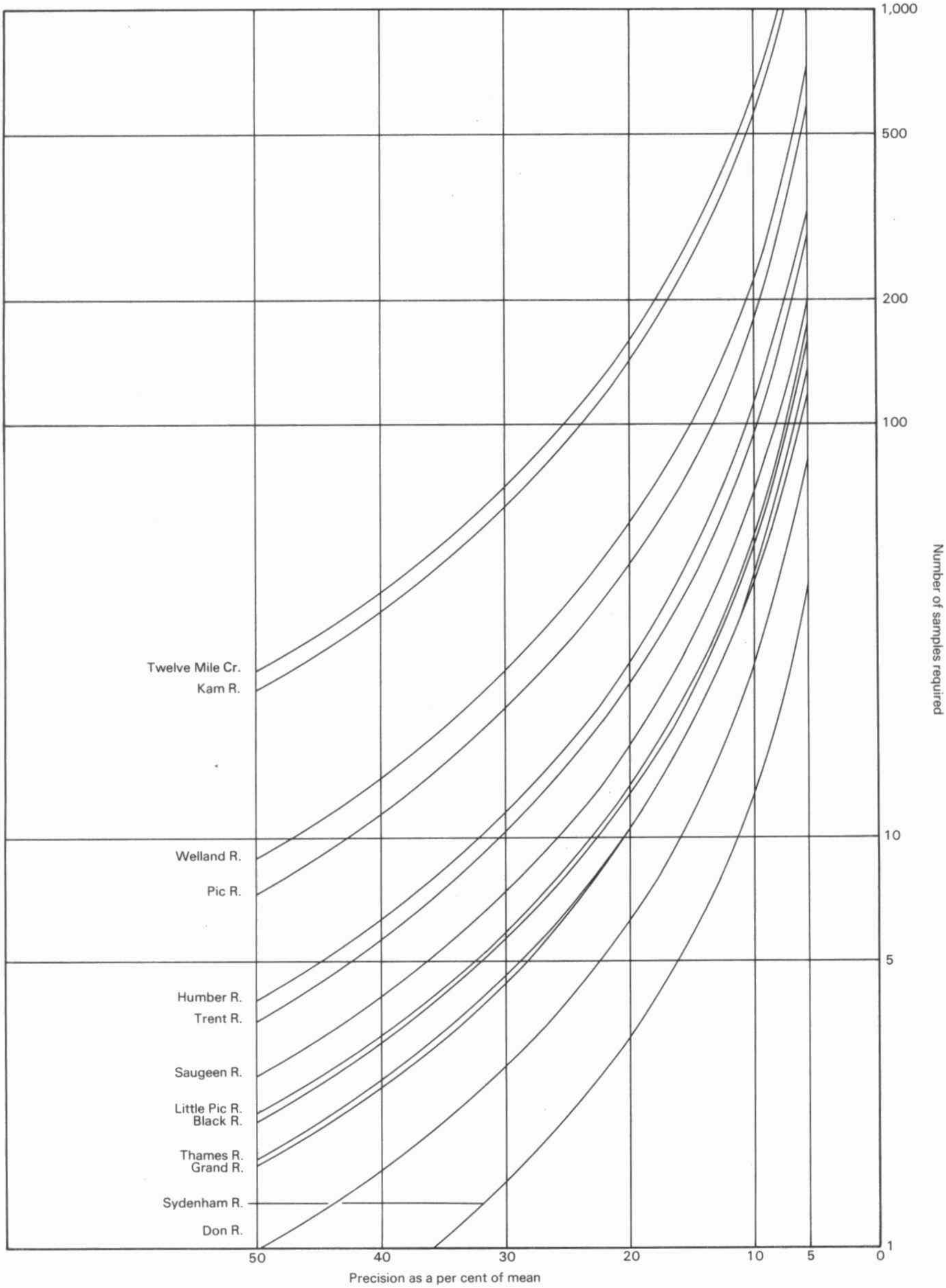


Figure 5b. Annual sampling frequency requirements to achieve varying levels of loading precision: nitrate–nitrogen.

4.0 SUMMARY AND CONCLUSIONS

Supplementary monitoring undertaken at the outlets of fifteen Ontario tributaries known to contribute comparitively high and variable phosphorus loads to the Great Lakes has enabled the acquisition of a significantly improved water-quality data base. This water-quality data base has been used in conjunction with streamflow records to compute tributary loading estimates. A corresponding improvement in loading estimates is apparent when the precision of phosphorus loadings computed with these data are compared with phosphorus loads computed from the historic water-quality data base. Continuation of the enhanced monitoring will provide a high standard of data quality and monitoring uniformity (i.e. sampling method, sample collection frequency and water-quality parameter coverage) to enable confident future comparisons of water-quality measurements and pollutant loading estimates.

Additional site-specific refinement of sampling strategy (i.e. sample collection frequency and water-quality parameter measurement) is proposed to optimize resource allocation at the 15 aforementioned monitoring stations and to aid in providing for further enhancement of future monitoring at two additional Great Lakes tributaries, the Ausable and Nottawasaga rivers.

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